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With amended claims.

(54) Title: PRINTING METHOD AND INK COMPOSITIONS THEREFOR

(57) Abstract

There is provided ink compositions each comprising 3 % by weight of each of standard dyes Solvent Yellow 83, Solvent Blue 44 and Solvent Red 127 in a solvent composition comprising 50 % by volume of each of 2–propylene glycol 1–methyl ether and methanol. The resulting filtered solutions were loaded into ink jet cartridges which were installed in an ink jet printing machine. Anodized aluminium sheet having a uniformly anodized surface is printed in the ink jet printing machine. The printed sheet is immersed in boiling water for ten minutes to fix the dye in the surface of the sheet, the print exhibiting sharp printing approaching photolithographic resolution and superior to average screen prints, with reduced bleeding and migration.

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PRINTING METHOD AND INK COMPOSITIONS THEREFOR

This invention relates to a printing method and ink compositions therefor.

This invention has particular but not exclusive application to printing of aluminium and alloy sheet, and for illustrative purposes reference will be made to such application. However, it is to be understood that this invention could be used in other applications, such as printing of microporous surfaces generally.

In the printing of aluminium and aluminium alloy sheet, use is made of the porous adherent oxide layer to absorb a printing medium. In general, the printing medium comprises dye or pigment inks, applied by one of two processes, screen printing or photolithography. In screen printing, the aluminium or other sheet is anodised using conventional anodising process, and prior to pore closure of the anodised surface the required image is printed on the surface by screen printing using paste-borne dyes. The dye component migrates into the porous anodized surface and is fixed therein by immersing the plate in boiling water, with or without fixing salts. If multiple colour printing is required, the screen printing process is repeated for each colour after initial dye set up of the preceding colour has occurred and prior to fixing.

The screen printing process is complicated, particularly for multiple colour work, and requires considerable operator skill. Only one colour can be printed at a time. For each colour, a separate screen must be cut. A common difficulty in

screen printing a metal sheet is in maintaining sharp resolution of the image, resolution being reliant on accurate indexing of the screens, accurate cutting of the screens, and the use of fine screens for fine work. Fine screens tend to gum and may become unusable during the print run, requiring preparation of a new screen.

Photolithographic processes offer greater precision. Anodised plate with open pores is coated with a light sensitive curable polymer composition or photo resist emulsion, usually sensitive to ultraviolet light. The sensitised plate is then exposed through a lithographic film, diazo film, cutting film, plotter film, tracing paper or other mask. The unexposed composition or emulsion is then washed off the plate. The plate is dried and then flooded with dye solution to impregnate the unexposed areas with dye. The exposed resist material is then dissolved off the plate, whereafter the process may be repeated for subsequent colours. Again the image may be fixed or sealed by immersing the plate in boiling water with sealing salts if required.

However, the process requires multiple process steps for multicolour printing. The photo resist materials are expensive and intractable materials to handle, requiring considerable skill in their handling and use. Each colour or separation requires the manufacture of a separate mask, offering multiple possibilities for error. The time required, skill level needed and difficulty in automating the process, and the costs of masks make photolithographic processes suitable for use in metal printing where a premium price may be paid.

Dye compositions for metal printing must have adequate penetration into the open pore of the generally oxidized metal surface to transport the chromophoric material into the oxide later, without excessive migration. As used hereinafter the term migration should be taken to means the diffusion or other transfer of dye from the point of application to an adjacent pixel or portion of the surface. Accordingly it has generally been accepted that metal printing must employ the paste cover or immersion dyeing techniques of screen printing and photographic methods as hereinbefore described.

Both prior art processes are expensive, particularly for small runs, and have multiple opportunities for error in multicolour applications. Both also create environmentally pollution in the form of residues and waste liquors which must be disposed of.

Ink jet printing is a common printing process for home and office use, offering low capital cost and near laser print resolution. The resolution achievable with ink jet printers of common manufacture approaches that of photolithographic processes for printing paper and exceeds that of screen printing processes for all but the thinnest and most intractable masks. However, ink jet printing is not suitable for printing a metal sheet since the dyes are incapable of being absorbed into the microporous metal surface of, for example, an anodized aluminium sheet.

The present invention aims to substantially alleviate at least one of the above disadvantages and to provide a metal printing process and dyes therefor which will be reliable and

efficient in use. Other objects and advantages of this invention will hereinafter become apparent.

With the foregoing and other objects in view, this invention in one aspect resides broadly in a printing method for open pore surfaces comprising printing of said surface with an ink comprising a chromophoric substance and an organic solvent therefor capable of solvating said dye in an amount of greater than 10g/L and being of boiling point suitable for use in an ink jet printing head.

It has been surprisingly determined that inks in accordance with the present invention permit ink jet printing of microporous surfaces such as an anodised aluminium sheet. It is speculated that the water-based inks used in ink jet printing have a surface tension which is too high to permit transport of the dye into the anodised surface of an aluminium sheet. The organic solvents of compositions in accordance with the present invention being of lower surface tension than the most modified water-based ink, achieve penetration in an anodised sheet which would not be expected on the basis of the water like viscosity of the inks.

However, it is envisaged that inks in accordance with the present invention may find application in other direct printing methods. As used hereinafter, reference to direct printing may be taken to mean any process which deposits ink on the surface of a substrate in the desired printing pattern without masks, screens or resists and includes processes such as plate printing, web offset printing or the like. However, it is preferred that the printing be by means of ink jet printing.

The ink jet printer apparatus may comprise a conventional ink jet printer having a suitable print medium path to accept a metal sheet, or at least be modified to accept a metal sheet. The ink jet printer may comprise a single print head whereby multiple passes are required for multicolour applications although it is preferred to use a three or four colour multiple print head machine. Typically the ink jet cartridges are loaded with yellow cyan and magenta inks in the case of three colour apparatus and with an additional black reservoir in the case of four colour printing apparatus.

The substrate is preferably selected from an aluminium or aluminium alloy sheet, preferably uniformly treated by anodizing to a standard suitable for printing although it is envisaged that methods in accordance with the present invention could be used on other surfaces having similar morphological surface characteristics such as oxide surface layer forming metals such as zinc and magnesium, passivated film metal surfaces such as nickel, cermet surfaces and ceramic surfaces. The aluminium surface may be anodized to a suitable thickness for printing, typically 10 to 25μ. Preferably, the surface treatment is provided shortly before printing to enable the ink to penetrate an open surface, the pores of anodised aluminium surfaces tending to close progressively on exposure to the atmosphere and close rapidly upon immersion in boiling water. However, it is envisaged that proprietary stabilised anodised surfaces may permit the use of long term stored stock when such stock is available.

The inks of the present method may be formed by solution

or suspension of chromophoric substances selected from pigments or dyes. Dyes may be selected from inorganic or organic metal complexes and organic dyes. For example, 1:1 or 1:2 metal complex of azo dyes, phthalocyanine dyes, or anthraquinone dyes may be used. Where pigments are used, these are preferably of a particle size of less than 2.0 microns to enable inkjet printing. For colour printing, it is usual to use dyes to produce inks of the CMY or CMYK set, that is, cyan, magenta, yellow and black. Examples of dyes which may be used to create inks of the present invention as the CMY set are the standard dyes Solvent Blue 44, Solvent Yellow 83, and Solvent Red 127.

The organic solvents may be selected from any organic solvents having the specified boiling point characteristics and the ability to solvate the dye or suspend the pigment. For ink jet printing the solvent is preferably selected to be of an appropriate boiling point or boiling range to accommodate the characteristics of available ink jet printing heads, although it is envisaged that the print head may be produced or modified to accommodate the ink. The solvent may be selected to be substantially non aggressive towards print head components currently in use. For example, ink reservoirs are commonly of plastic, requiring selection of a solvent which does not substantially attack the plastic.

Ink jet print heads, being generally adapted to use water-based inks, are adapted to use inks having a boiling point of about that of water. Such print heads commonly operate at temperatures of from 300 to 350°C to create the vapour bubble which projects the ink jet at the substrate. Accordingly the

solvent is preferably selected to be stable against liquid or vapour phase decomposition at the print head operating temperature, and to be capable of forming a jet propelling bubble in operation of the print head. The solvent preferably solvates the dye into an ink composition which is of similar viscosity to the water based inks used in conventional ink jet print heads.

The solvent may comprise a mixture of solvents to achieve the preferred characteristics. Preferably, the solvent mixtures have a relatively narrow boiling range. For example, the solvent mixture may comprise an azeotropic solvent mixture adapted to have a boiling point in the region of 90 to 110°C. Alternatively, the solvent mixture may comprise a mixture of two or more solvents having a preferably narrow boiling range between 90 and 110°C.

In solvent mixtures, there may be used a relatively low boiling solvent of low viscosity and relatively high vapour pressure, and a relatively high boiling solvent of sufficient viscosity to provided the ink with rheological properties suitable for ink jet printing in combination with the selected chromophoric substance and the low boiling solvent. The respective solvents are preferably selected to be of relatively low toxicity. Water miscibility may also be advantageous.

The solvents may be selected from alcohols, ethers, esters, polyol-ethers, aliphatic, branched or cyclic alkanes, alicyclic or aliphatic ketones, aromatic solvents or the like. Preferably, the ink is dye based and each of the solvents is selected to dissolve the dye at least in combination. The ink

may be prepared by dissolution of the dye in the solvent. This may be accompanied by stirring at a temperature of from 40 to 60°C for the preferred dyes. The solution may be cooled prior to preferably filtering to a particle size of less than 2.0μ.

The present applicant has unexpectedly determined that the inks of the present invention permit increased penetration of the dyestuff or pigment into the oxide layer of the metal sheet whilst exhibiting less migration than conventional volatile-solvent based dye. The reason for this is not clearly understood but may relate to the chromatographic mobility of the dye or pigment in the anodised layer wherein the organic solvents of the present invention function as an eluting solvent, the solvent front extending beyond the dye front. It is speculated that the ink impacts on the surface of anodised aluminium sheet and is rapidly eluted into the thickness of the anodised layer, whereafter the advancing solvent front flashes off. Thus the dye is rapidly transported into the surface at a very high effective concentration in excess of the solubility of the dye, with reduced migration and reduced tendency for bleeding in the sealing process.

Accordingly, in a further aspect, this invention resides in an ink composition comprising a dye dissolved in a solvent comprising a chromophoric substance and an organic solvent therefor capable of solvating said dye in an amount of greater than 10g/L and being of boiling point suitable for use in an ink jet printing head.

In order that this invention may be more readily understood and put into practical effect, reference will now be

made to the following example which illustrates a preferred embodiment of the invention.

EXAMPLE 1

An ink composition was prepared comprising 3% by weight of each of standard dyes Solvent Yellow 83 (SANDOZ SAVINYL YELLOW RLSN), Solvent Blue 44 (SANDOZ SAVINYL BLUE GLS) and Solvent Red 127 (SANDOZ SAVINYL PINK 6BLS) were dissolved in a solvent composition comprising 50% by volume of each of 2-propylene glycol 1-methyl ether and methanol. Solvation of the respective dyes in the solvent was achieved by heating the mixtures to 50°C with stirring. The mixtures were allowed to cool before decanting and filtering twice to a final grade of less than 1.6 microns. The resulting filtered solutions were loaded into ink jet cartridges which were installed in an ink jet printing machine.

Anodized aluminium sheet of 0.5mm thickness having a uniformly anodized surface of thickness nominally of 18 to 20 μ was fed into the ink jet printing machine, which was operated under the control of a personal computer to print a test pattern on the sheet using ink from the ink cartridge loaded with dye solution in accordance with the present invention. The printed sheet was removed from the printing machine and immersed in boiling water for ten minutes to fix the dye in the surface of the sheet.

Aluminium sheet printed in accordance with the foregoing embodiment exhibited sharp printing approaching photolithographic resolution and superior to average screen prints, with reduced bleeding and migration.

It will of course be realised that while the above has been given by way of illustrative example of this invention, all such and other modifications and variations thereto as would be apparent to persons skilled in the art are deemed to fall within the broad scope and ambit of this invention as defined in the claims appended hereto.

CLAIMS

1. A printing method for open pore surfaces comprising printing of said surface with an ink comprising a chromophoric substance and an organic solvent therefor capable of solvating said dye in an amount of greater than 10g/L and being of boiling point suitable for use in an ink jet printing head.

2. A printing method according to Claim 1, wherein said printing is by means of ink jet printing.

3. A printing method according to Claim 2, wherein said surface is an anodised aluminium or aluminium alloy sheet surface.

4. A printing method according to any one of Claims 2 and 3, wherein said ink comprises cyan, magenta, yellow and black inks loaded into ink jet cartridges of a multiple print head colour ink jet printing apparatus.

5. A printing method according to any one of the preceding Claims, wherein said ink comprises a dye selected from inorganic or organic metal complexes and organic dyes.

6. A printing method according to Claim 5, wherein said dye is an organic dye selected from 1:1 or 1:2 metal complex of azo dyes, phthalocyanine dyes, or anthraquinone dyes.

7. A printing method according to Claim 6, wherein at least

the CMY dye set is used, and wherein the respective inks are based on the standard dyes Solvent Blue 44, Solvent Yellow 83, and Solvent Red 127.

8. A printing method according to ant one of the preceding Claims, wherein said ink or inks have a boiling range suitable for use with ink jet printing heads having an operating temperature of from 300 to 350°C.

9. A printing method according to Claim 8, wherein said ink comprises solvent selected to be stable against liquid or vapour phase decomposition at the print head operating temperature.

10. A printing method according to Claim 9, wherein the solvent is selected to provide an ink having a viscosity similar to that of the water based inks used in conventional ink jet printing heads.

11. A printing method according to Claim 10, wherein said solvent comprises a mixture of solvents of relatively narrow boiling range.

12. A printing method according to Claim 11, wherein said mixture of solvents comprises an azeotropic solvent mixture selected to have a boiling point in the region of 90 to 110°C.

13. A printing method according to Claim 11, wherein said

mixture of solvents comprises a mixture of two or more solvents having a narrow boiling range falling in the band between 90 and 110°C.

14. A printing method according to any one of Claims 12 and 13, wherein said solvent mixture comprises a relatively low boiling solvent of low viscosity and relatively high vapour pressure, and a relatively high boiling solvent of sufficient viscosity to provided the ink with rheological properties suitable for ink jet printing in combination with the selected chromophoric substance and the low boiling solvent.

15. A printing method according to Claim 14, wherein said solvents are selected from alcohols, ethers, esters, polyol-ethers, aliphatic, branched or cyclic alkanes, alicyclic or aliphatic ketones, aromatic solvents or the like.

16. A printing method according to Claim 15, wherein said solvent mixture comprises 50% by volume of each of 2-propylene glycol 1-methyl ether and methanol.

17. An ink composition comprising a dye dissolved in a solvent comprising a chromophoric substance and an organic solvent therefor capable of solvating said dye in an amount of greater than 10g/L and being of boiling point suitable for use in an ink jet printing head.

18. An ink composition according to Claim 17, wherein said dye

is selected from inorganic or organic metal complexes and organic dyes.

19. An ink composition according to Claim 18, wherein said dye is an organic dye selected from 1:1 or 1:2 metal complex of azo dyes, phthalocyanine dyes, or anthraquinone dyes.

20. An ink composition according to Claim 17, wherein said dye is selected from standard dyes Solvent Blue 44, Solvent Yellow 83, and Solvent Red 127.

21. An ink composition according to Claim 20, wherein said solvent comprises a mixture of solvents of relatively narrow boiling range.

22. An ink composition according to Claim 21, wherein said solvents are selected from alcohols, ethers, esters, polyol-ethers, aliphatic, branched or cyclic alkanes, alicyclic or aliphatic ketones, aromatic solvents or the like.

23. An ink composition according to Claim 22, wherein said solvent mixture comprises 50% by volume of each of 2-propylene glycol 1-methyl ether and methanol.

24. An ink composition according to any one of Claims 17 to 23, prepared by dissolution of the dye in the solvent with stirring at a temperature of from 40 to 60°C, cooling the solution, and filtering to a particle size of less than 2.0µ.

AMENDED CLAIMS

[received by the International Bureau on 12 March 1998 (12.03.98);
original claims 1-24 replaced by new claims 1-21 (3 pages)]

1. An ink jet printing method for printing an open pore oxidized aluminium surface including the steps of:

selecting an ink jet printing apparatus;

loading said apparatus with an ink formed of a dye and an organic solvent capable of solvating said dye in an amount of greater than 10g/L and being of boiling range selected for use with said ink jet printing apparatus, said solvent comprising a mixture of a low boiling solvent, and a high boiling solvent of sufficient viscosity to provide the ink with rheological properties suitable for use in said ink jet printing apparatus, and

printing said surface.

2. A printing method according to Claim 1, wherein said surface is selected from an anodised aluminium or aluminium alloy sheet surface.

3. A printing method according to any one of Claims 1 and 2, wherein said ink comprises cyan, magenta, yellow and black dye inks loaded into ink jet cartridges of a multiple print head colour ink jet printing apparatus.

4. A printing method according to any one of the preceding Claims, wherein said ink comprises a dye selected from inorganic or organic metal complexes and organic dyes.

5. A printing method according to Claim 4, wherein said dye is an organic dye selected from 1:1 or 1:2 metal complex of azo dyes, phthalocyanine dyes, or anthraquinone dyes.

6. A printing method according to Claim 5, wherein at least the CMY dye set is used, and wherein the respective inks are based on the standard dyes Solvent Blue 44, Solvent Yellow 83, and Solvent Red 127.

7. A printing method according to any one of the preceding

Claims, wherein said ink or inks have a boiling range suitable for use with ink jet printing heads having an operating temperature of from 300 to 350°C.

8. A printing method according to Claim 7, wherein said ink comprises solvent selected to be stable against liquid or vapour phase decomposition at the print head operating temperature.

9. A printing method according to Claim 8, wherein the solvent is selected to provide an ink having a viscosity similar to that of the water based inks used in conventional ink jet printing heads.

10. A printing method according to any one of the preceding Claims, wherein said mixture of solvents comprises an azeotropic solvent mixture selected to have a boiling point in the region of 90 to 110°C.

11. A printing method according to any one of Claims 1 to 10, wherein said mixture of solvents comprises a mixture of two or more solvents having a narrow boiling range falling at least partially in the band between 90 and 110°C.

12. A printing method according to any one of the preceding Claims, wherein said solvents are selected from alcohols, ethers, esters, polyol-ethers, aliphatic, branched or cyclic alkanes, alicyclic or aliphatic ketones, aromatic solvents or the like.

13. A printing method according to Claim 14, wherein said solvent mixture comprises 50% by volume of each of 2-propylene glycol 1-methyl ether and methanol.

14. An ink formed of a dye and an organic solvent capable of solvating said dye in an amount of greater than 10g/L and being of boiling range selected for use with an ink jet printing

apparatus, said solvent comprising a mixture of a low boiling solvent, and a high boiling solvent of sufficient viscosity to provide the ink with rheological properties suitable for use in said ink jet printing apparatus.

15. An ink composition according to Claim 14, wherein said dye is selected from inorganic or organic metal complexes and organic dyes.

16. An ink composition according to Claim 15, wherein said dye is an organic dye selected from 1:1 or 1:2 metal complex of azo dyes, phthalocyanine dyes, or anthraquinone dyes.

17. An ink composition according to Claim 15, wherein said dye is selected from standard dyes Solvent Blue 44, Solvent Yellow 83, and Solvent Red 127.

18. An ink composition according to Claim 14, wherein said solvent comprises a mixture of solvents of relatively narrow boiling range.

19. An ink composition according to Claim 18, wherein said solvents are selected from alcohols, ethers, esters, polyol-ethers, aliphatic, branched or cyclic alkanes, alicyclic or aliphatic ketones, aromatic solvents or the like.

20. An ink composition according to Claim 19, wherein said solvent mixture comprises 50% by volume of each of 2-propylene glycol 1-methyl ether and methanol.

21. An ink composition according to any one of Claims 14 to 20, prepared by dissolution of the dye in the solvent with stirring at a temperature of from 40 to 60°C, cooling the solution, and filtering to a particle size of less than 2.0μ.

INTERNATIONAL SEARCH REPORT

International Application No.
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A. CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: C09D 011/02, 011/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D 011/02, 011/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT : DYE, PIGMENT OR CHROMOPHOR; ALUMINIUM; ALCOHOL, METHANOL OR ETHER; JET PRINTER

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A, 96/23844 (THE GENERAL ELECTRIC COMPANY PLC), 8 August 1996 Page 6, lines 4-28; claims 1-3, 8-9 and 21-23	1-24
X	US, A, 4021252 (D.P. BANCZAK ET AL) 3 May 1977 claims 1-5, 13 and 15-23	1-24
X	AU, A, 91133/82 (GESTETNER MANUFACTURING LIMITED), 28 July 1983 claims 1-4 and 9-10	1-24
X	US, A, 5258065 (TOSHIKI FUJISAWA) 2 November 1993 claims 1-10	1-24

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

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Date of the actual completion of the international search	Date of mailing of the international search report
24 December 1997	14 JAN 1998

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INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 97/00827

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4732613 (MAKOTO SHIOYA ET AL) 22 March 1988 column 1, line 62 - column 2, line 11; column 2, line 63 - column 3, line 25; and example 1a	1-24
X	FR, A, 2359191 (LORILLEUX LEFRANC INTERNATIONAL), 24 March 1978 whole document	1-24
A	EP, A, 466345 (VIDEOJET SYSTEMS INTERNATIONAL, INC.) 15 January 1992 whole document	1-24
X	Derwent Abstract Accession No. 94-260747, Class A97, and JP, A, 6-192612 (PENTEL KK), 12 July 1994 abstract	1-24
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X	Derwent Abstract Accession No. 95-034215, Class A82, and RO, B1, 107967 (CENT CERC PROTECTII ANTICORDSIVELACURI), 31 January 1994 abstract	1-24

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/AU 97/00827

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
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EP	466345	AU	78312/91	AU	70233/94	CA	2043246
		JP	4248882				
AU	91133/82	BE	895377	DE	3246337	DK	5376/82
		FR	2519996	GB	2113701	JP	58127771
		NL	8204760	SE	8206930	ZA	8208900

END OF ANNEX